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1 Coordination behavior and transformations of thienyl
2 substituted diacetylenes upon coordination to
3 $\text{Os}_3\text{H}_2(\text{CO})_{10}$

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16 **Abstract:** The reaction between 2- and 3-thienyl substituted 1,3-butadiynes and the electron deficient
17 osmium cluster $\text{Os}_3\text{H}_2(\text{CO})_{10}$ yields trinuclear coordination products, associated with transformations of
18 the diacetylene ligands. Depending on the heteroaryl end groups, osmium clusters with both closed and

open Os-triangle core were formed. The reaction between $\text{Os}_3\text{H}_2(\text{CO})_{10}$ and 1,4-bis(2-thienyl)butadiyne yielded $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}\{(\mu\text{-}\eta\text{-}(\text{C}_4\text{H}_3\text{S})(\text{C}_8\text{H}_4\text{S}))\}]$ (1) and $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}\{(\mu_3\text{-}\eta^2\text{-}\eta^1\text{-}\eta^1\text{-}(\text{SC}_7\text{H}_4)\text{C}(\text{SC}_4\text{H}_3))\}]$ (2) whereas in the analogous case of 1,4-bis(3-thienyl)butadiyne the main coordination product was found to be $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}\{(\mu\text{-}\eta\text{-}(\text{C}_4\text{H}_3\text{S})(\text{C}_8\text{H}_4\text{S}))\}]$ (3). Compounds 1-3 were stable in air, but lost carbon monoxide upon prolonged heating. Thermal decarbonylation of 1 under N_2 yielded a mixture of $[\text{Os}_3(\mu\text{-H})(\text{CO})_9\{(\mu_3\text{-}\eta^3\text{-}(\text{C}_4\text{H}_3\text{S})(\text{C}_8\text{H}_4\text{S}))\}]$ (4) and $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_9\{(\mu_3\text{-}\eta^1\text{-}\eta^1\text{-}(\text{C}_4\text{H}_3\text{S})(\text{C}_8\text{H}_3\text{S}))\}]$ (5). Thermal decarbonylation of 2 yielded $[\text{Os}_3(\mu\text{-H})(\text{CO})_9\{(\mu_3\text{-}\eta^3\text{-}(\text{C}_4\text{H}_3\text{S})(\text{C}_8\text{H}_4\text{S}))\}]$ (6), while thermal decarbonylation of 3 yielded $[\text{Os}_3(\mu\text{-H})(\text{CO})_9\{(\mu_3\text{-}\eta^3\text{-}(\text{C}_4\text{H}_3\text{S})(\text{C}_8\text{H}_4\text{S}))\}]$ (7). A reaction involving 3 with CF_3COOH affords as the main cluster product the known cluster $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\text{O}_2\text{CF}_3)]$ (8) and, unusually, permits the isolation and characterisation of the novel organic molecule $[(\text{C}_4\text{H}_3\text{S})(\text{C}_8\text{H}_4\text{S})(\text{OCF}_3)]$ (9) cleaved from the parent cluster. The structures of the new compounds were established by single crystal X-ray studies and spectroscopic methods, and supported by density functional theory.

Introduction

The fundamental alkyl-cluster interactions have been extensively studied, particularly those of osmium and ruthenium carbonyl clusters.¹ Much of the current interest has emphasized the studies of poly-yne interactions, which offer great variety of coordination modes due to the extended carbon backbone, along with the opportunity to link small cluster units with a poly-yne ligand.² Thermolysis reactions between carbonyl clusters and a variety of functionalized poly-ynes can involve either metal-metal bond cleavage, alkyne bond activation, intramolecular cyclization or ligand coupling to give cluster products with varying nuclearity.^{2e,3}

In reactions between functionalised diynes and osmium clusters such as $\text{Os}_3\text{H}_2(\text{CO})_{10}$ and $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$, the cluster nuclearity is maintained, but changes in the cluster core geometry and ligand rearrangements are possible.⁴ The latter phenomenon has been studied in particular in the case of

43 hydrido clusters, where the hydride transfer from the cluster is likely to initiate ligand rearrangements.
44 The nature of the terminal substituents of the diyne determines the result of the ligand rearrangement.^{4b,5}

45 Reactions of diynes with $\text{Os}_3\text{H}_2(\text{CO})_{10}$ tend to afford cyclisation of the ligand⁴ which is thought to
46 proceed *via* an abstraction of a hydrogen atom attached to the β -carbon atom of the diyne which leads
47 to the formation of a bond between the β -carbon atom and the third carbon of the $-\text{C}_2-\text{C}_2-$ diyne
48 group.^{2a,b} In the case of $\text{HOH}_2\text{CC}\equiv\text{C}-\text{C}\equiv\text{CCH}_2\text{OH}$ this process leads the formation of a cyclic product
49 incorporating a furan ring,^{4a} while the ligand $\text{PhC}\equiv\text{C}-\text{C}\equiv\text{CPh}$ gives an indenyl fragment as the
50 rearrangement product.⁵ The cluster $[\text{Os}_3\text{H}(\text{CO})_{10}(\eta^1:\eta^1-\text{OC}_4\text{H}_2\text{CCH}_3)]$ has been shown to undergo an
51 aldol condensation reaction with aromatic aldehydes.⁶ Similar cyclisations products have also been
52 observed in the reaction of $\text{Os}_3\text{H}_2(\text{CO})_{10}$ with other substituted diynes $\text{RC}\equiv\text{C}-\text{C}\equiv\text{CR}'$ ($\text{R}=\text{Ph}$,
53 $\text{R}'=\text{CH}_2\text{NHPh}$; $\text{R}=\text{Ph}$, $\text{R}'=\text{CH}_2\text{NHCH}_2\text{Ph}$; $\text{R}=\text{R}'=\text{CH}_2\text{NHPh}$; $\text{R}=\text{R}'=\text{C}_5\text{H}_4\text{N}$).^{4b,7} Reactions involving
54 $\text{Os}_3\text{H}_2(\text{CO})_{10}$ and $\text{Me}_3\text{SiC}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3$ do not result in cyclisation products due to the 1,2- shift of the
55 SiMe_3 stabilising the ethynyl ligand.⁸ Similarly, a 1,2-shift of one of the ferrocenyl groups along the
56 butadiyne chain has been suggested to account for the products of the reaction of $\text{FcC}\equiv\text{C}-\text{C}\equiv\text{CFc}$ with
57 $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-}\eta^2\text{-NC}_5\text{H}_4)]$.⁹

58 Hydrodesulfurisation (HDS) is the catalytic process by which the sulfur present in crude oil and
59 petroleum distillates is removed which leads to a greener process *via* the reduction of SO_2 emission.
60 Commercial heterogeneous HDS catalysts consist of metal sulfide crystallites on a support surface.
61 However there is little understanding of the active site, or the chemical processes occurring. For this
62 purpose carbonyl clusters and organosulfur compounds have been used as models in understanding the
63 hydrosulfurisation adsorption and desulfurisation phenomena used in treatment of crude oil.¹⁰ Increased
64 catalytic activity has been observed, particularly toward thiophenes, when late transition metals (group
65 8) are employed.^{10b}

66 In general, reactions between a late transition metal carbonyl cluster and an organosulfur compound
67 such as a functionalised thiophene result in an insertion of a metal cluster fragment into a C-S bond,

68 along with desulfurisation of the heterocycle.¹⁰ In contrast, reactions between thiophenes,
69 benzothiophene or thietane and a triosmium carbonyl cluster results in a C-H bond activation¹¹ which
70 occurs in preference to the C-S bond cleavage seen in reactions of thiophenes with ruthenium and
71 ferrocene carbonyl clusters.¹² Although C-S bond cleavage reactions have not been observed in reactions
72 between thiophenes and triosmium carbonyl clusters, ring opening reactions occur in reactions between
73 the activated osmium cluster, Os₃(CO)₁₀(NCMe)₂, and selenophene and tellurophene.^{12b} Because of the
74 importance of HDS systems and the versatility of functionalised diynes it was considered valuable to
75 investigate the reaction chemistry of thienyl butadiynes with osmium clusters.

76 Room temperature reaction of 1,4-bis(2-thienyl)butadiyne with the labile acetonitrile cluster
77 Os₃(CO)₁₀(NCMe)₂, yields coordination products where the thienyl functionalities remain intact,
78 yielding a typical μ_3 - η^2 coordination product and a novel two stranded linear osmium cluster.¹³ These
79 results are echoed in the reaction between Os₃(CO)₁₀(NCMe)₂ and 1,4-bis(ferrocenyl)-1,3-butadiyne,
80 which gives an open triosmium cluster coordinated as a linear chain to the triple bonds of the ligand
81 along with the expected coordination of the ligand as a triple bridge to a triangle of osmium.¹⁴ In
82 comparison, the reaction of 1,8-bis-(ferrocenyl)-octatetrayne with Os₃H₂(CO)₁₀ has been shown to yield
83 products involving trans-hydrogenation and cyclisations with the incorporation of CO.^{3e}

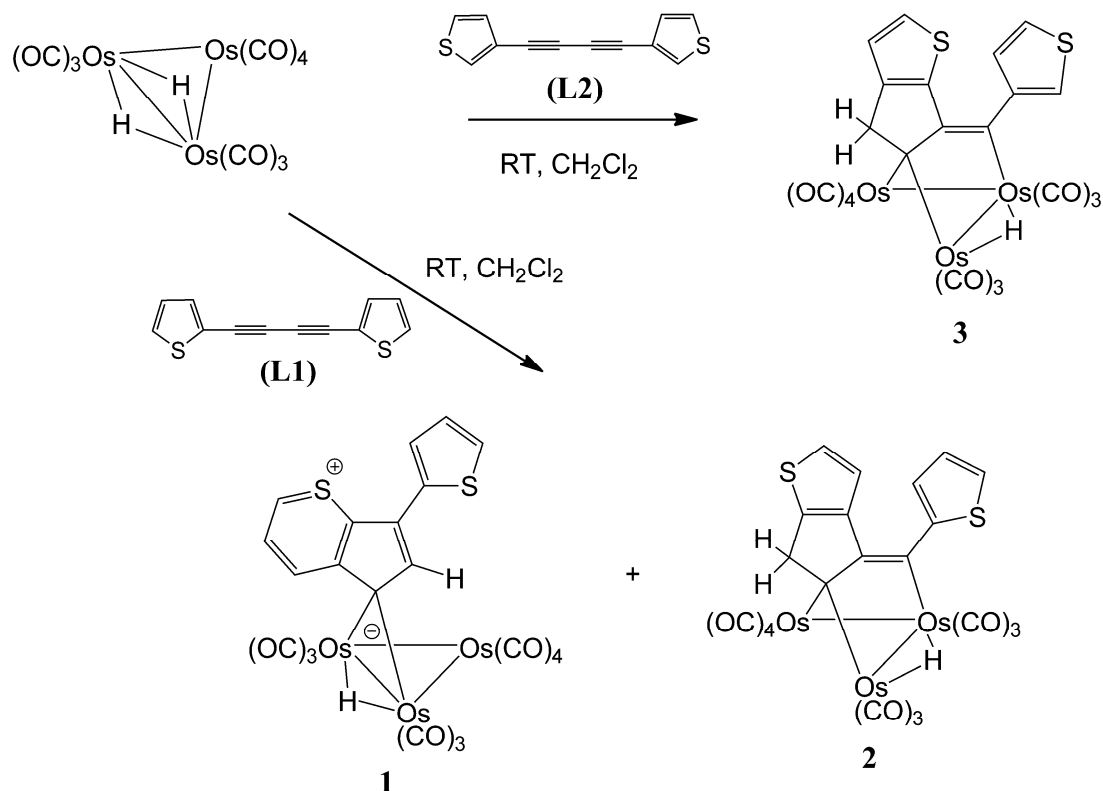
84 In this paper we extend the study of the reaction between osmium hydride, Os₃H₂(CO)₁₀ and diynes to
85 include thienyl functionalised 1,3-butadiynes. These reactions give products in which the diyne unit has
86 been transformed into a bicyclic ligand. Prolonged heating of these complexes resulted in carbonyl loss,
87 and in one instance, reaction with trifluoroacetic acid enabled the isolation of the bicyclic organic
88 compound. In all cases, the complexes were characterised spectroscopically and by single crystal X-ray
89 crystallography.

90 Results and Discussion

91 Synthesis of 1 and 2.

92 An equimolar reaction between Os₃H₂(CO)₁₀ and 1,4-bis(2-thienyl)butadiyne (**L1**) at room
93 temperature affords [Os₃(μ -H)(CO)₁₀{ μ - η -(C₄H₃S)(C₈H₄S)}] (**1**) as a major dark green product in 50%

94 yield, together with $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}\{\mu_3\text{-}\eta^2\text{-}\eta^1\text{-}\eta^1\text{-}(\text{SC}_7\text{H}_4)\text{C}(\text{SC}_4\text{H}_3)\}]$ (**2**) and a number of other
 95 unidentified species (Scheme 1). Compound **1** is a dark green material, soluble in medium polarity
 96 organic solvents, and insoluble in hydrocarbons. **2** is an orange solid, at least partially soluble in all
 97 common organic solvents.



98

99

100 **Scheme 1.** Reaction of $\text{Os}_3(\text{H})_2(\text{CO})_{10}$ with dithienylbutadiynes

101 The room temperature ^1H NMR spectrum of **1** showed aromatic resonances, a resonance downfield at
 102 δ 9.60 due to the protonated carbon of the cyclopentene group fused to the thiopyran and a single
 103 (integral 1H) hydride resonance at δ -14.82. At 220K the ^{13}C NMR spectrum revealed ten aromatic
 104 resonances, along with one resonance at δ 63.07 due to the carbon bridging the Os-Os edge. There are a
 105 further six resonance in the ^{13}C NMR spectrum associated with the terminal carbonyls of the cluster
 106 which, due to the symmetry plane in the molecule produces six chemically inequivalent environments
 107 resulting in a 2:2:2:2:1:1 signal ratio. At 298K, the ^{13}C NMR spectrum was missing two carbonyls,
 108 suggesting an exchange process which either broadens these signals or renders some of the carbonyls

109 equivalent. The FAB-MS spectrum along with the IR spectrum obtained for **1** were unremarkable
110 exhibiting the expected molecular ion and absorptions for terminal $\nu(\text{CO})$, respectively.

111 The solid state molecular structure of **1** was determined by single-crystal X-ray diffraction from dark
112 green crystals grown by slow evaporation of a dichloromethane solution (Figure 1, Table 1). The cluster
113 consists of a closed 48 electron osmium triangle, where Os(1) is coordinated by four terminal CO
114 ligands, while Os(2) and Os(3) are coordinated by three terminally bound carbonyls and bridged by a
115 hydride and η^1 alkylidene ligand. A novel cyclization of the bis(thiophene) ligand has been effected
116 resulting in the formation of a cyclopentene group fused to the thiopyran by incorporation of the carbon
117 atoms from the original alkyne unit. The six-membered ring is a product of ring expansion on one of the
118 original thiophene ligands with bond lengths varying from 1.368(8) to 1.690(5) Å, with the carbon-
119 sulfur bond lengths being approximately equal. The cyclised hydrocarbon is almost entirely planar and
120 lies perpendicular to the Os(2)-Os(3) axis with the ligand anchored via an alkylidene interaction with
121 almost equal distances of 2.230(5) and 2.235(5) Å for Os(2)-C(11) and Os(3)-C(11) respectively. In this
122 coordination mode the newly formed cyclopentene moiety donates only two electrons via the alkylidene
123 interaction from C(11). With a single electron donated from the bridging hydride the cluster would
124 remain electron deficient, unless charge separation is taken into account, with a positive charge being
125 associated with the S-centre of the six-membered ring of the cyclized hydrocarbon and an electron being
126 transferred to the cluster. Zwitterionic cluster complexes have been reported previously.¹⁵

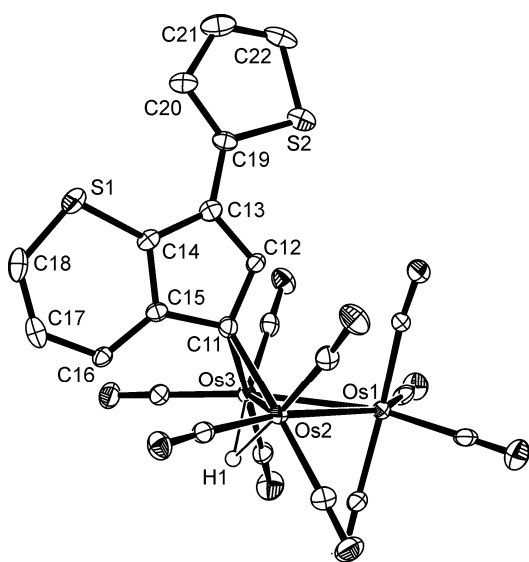


Figure 1. ORTEP plot (50% displacement ellipsoids) of the X-ray structure of **1**.

To the best of our knowledge, the formation of this alkylidene complex is completely unprecedented in the field of osmium cluster chemistry. The ring expansion, via insertion of a carbon atom of the diyne backbone into the adjacent double bond of the thiophene ring, coupled with the ligand cyclization observed, leads to a very novel product. The mechanistic pathway as to its generation remains unclear but is related to the formation of a cyclic product incorporating a furan ring for the reaction between $\text{Os}_3\text{H}_2(\text{CO})_{10}$ and $\text{HOH}_2\text{CC}\equiv\text{C}-\text{C}\equiv\text{CCH}_2\text{OH}$.^{4a}

In the reaction to form compound **1**, small amounts of another product, compound **2**, were formed. Compound **2** could not be obtained pure by chromatographic separation. The crude material contained a number of (probably isomeric) species. Although attempts to chromatographically separate these compounds failed, partial evaporation of a dichloromethane solution of the mixture gave a number of small single crystals of **2**. These crystals were suitable for single crystal X-ray diffraction and limited spectroscopic analysis.

The room temperature ^1H NMR spectrum of **2** exhibited a broad, integral 3H multiplet and two integral 1H doublets in the aromatic region, an AB multiplet centred at δ 3.54 and a single hydride resonance at δ -16.94. The presence of an AB multiplet is consistent with a pair of inequivalent methylene protons on the cyclopentene ring. Lowering the temperature to 228K resulted in the broad

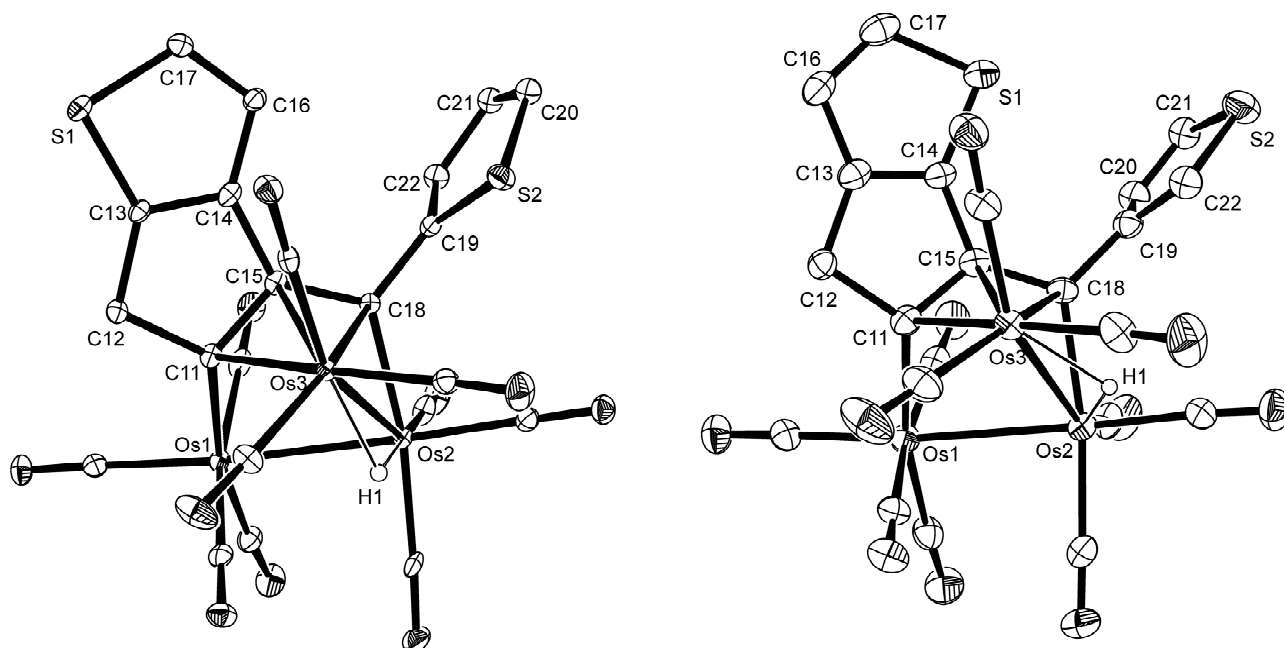
peak splitting into two sets of three sharp, well-resolved signals, and the hydride signal splitting into two (*ca.* 60:40 ratio). These results are most likely to be due to slow exchange between two conformers. Two conformers, differing by a 180° rotation of the thiophene ring, are noted in the solid state structure (*vide infra*).

The FAB-MS spectrum did not exhibit the molecular ion; however, a fragment ion arising due to the loss of one carbonyl, at m/z 1040, was observed. The IR spectrum was characterised by absorptions for terminal $\nu(\text{CO})$. Spectroscopic evidence leads to the conclusion that the formation of two fused five-membered rings, one containing a sulfur atom, has occurred. The formation is likely to proceed via ring opening and hydrogen translocation similar to that observed in an analogous reaction involving 1,4-diphenylbuta-1,3-diyne.⁵

The solid state molecular structure of **2** (Figure 2, Table 2) demonstrates that the metal framework of this compound consists of an open 50 electron triosmium unit, which is coordinated to the rearranged ligand system. The open triangular unit is also coordinated by ten terminal carbonyls and a bridging hydride between Os(2) and Os(3). The insertion of a hydride ligand from the parent cluster has been accompanied by the proton translocation, cyclization and ring fusion of the thiophene and alkyne units. One of the ring carbons, C(11), from the resulting substituted cyclopentathiophene ring has inserted into the Os(1)-Os(3) edge creating an Os₃C diamond-shaped core. The transformed ligand acts as a five-electron donor, bridging all three metal atoms through a carbene interaction from C(11) to Os(1) and Os(3), a π -interaction from C(15)-C(18) to Os(2) and a σ -bond from C(18) to Os(1). The Os(1)-C(11) bond distance is 2.198(5) Å, which is significantly shorter than the adjacent Os(3)-C(11) distance (2.317(5) Å). The bridging hydride could be located from the Fourier map, confirming the results from the ¹H NMR spectrum.

The bond lengths in the tricarbon bridge, C(11)-C(15) and C(15)-C(18) are 1.442(7) Å and 1.422(7) Å respectively, indicating considerable delocalisation. The C(12) vertex is identified as an sp³ centre bonded to two protons, which is in accordance with the ¹H NMR spectrum of **2**. The free thiophene ring is twisted out of the plane of the bicyclic component of the ligand, as unfavourable steric interactions

171 between the thiophene ring and H16 would result if the entire ligand was completely planar. This
172 thiophene ring is disordered (57:43) and thus bond metrics for this unit cannot be reliably obtained.



173
174

175 **Figure 2.** ORTEP plot (30% displacement ellipsoids) of the X-ray structure of **2** (left) and **3** (right).
176 Hydrogen atoms (except H1) and minor disorder components are omitted for clarity.

177 **Synthesis of 3.**

178 The reaction between Os₃H₂(CO)₁₀ and 1,4-bis(3-thienyl)butadiyne (**L2**), analogous to one involving
179 1,4-bis(2-thienyl)butadiyne, gives a single yellow product [Os₃(μ-H)(CO)₁₀{μ-η-(C₄H₃S)(C₈H₄S)}] (**3**)
180 (Scheme 1). The reaction was found to proceed notably slower than that involving 1,4-bis(2-
181 thienyl)butadiyne, as monitored by TLC and IR during the reaction; most of the parent cluster was
182 consumed only after 48 hours. Both crystalline and non-crystalline samples of **3** yielded similar
183 spectroscopic data, with no evidence of the existence of other structural isomers. The ¹H NMR spectrum
184 consisted of aromatic multiplets at δ 7.37–6.77 (5H), an AB signal at *ca.* δ 4.1 (2H) and a singlet at δ
185 -16.9 (1H). This spectrum is similar to that of **2**, strongly suggesting a similar coordination mode and
186 ligand transformation as for **2**. The IR spectrum (carbonyl region) of **3** was almost identical to that of **2**,
187 again consistent with the two species having similar structures.

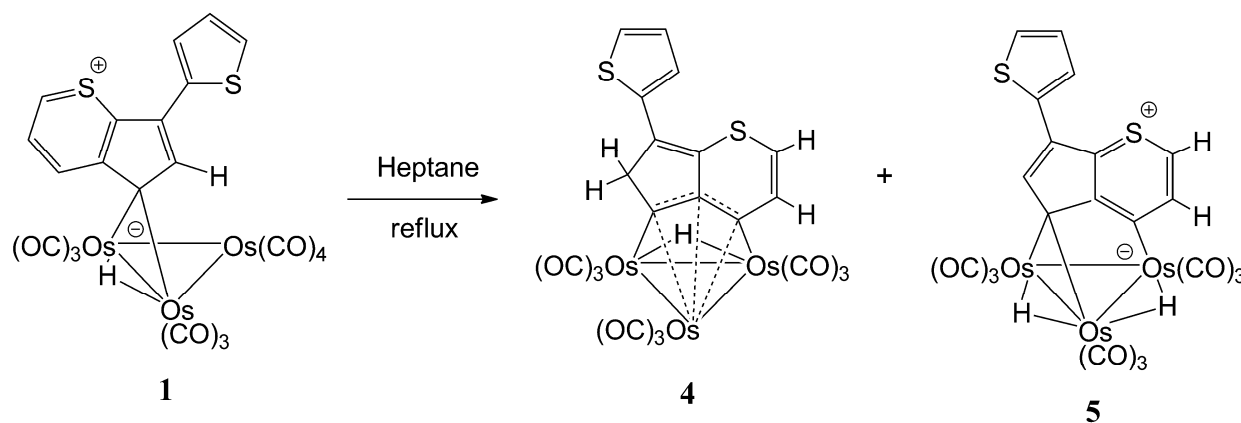
188 The solid state molecular structure of **3** (Table 2, Figure 2) is similar to that of **2**, consisting of a
189 diamond-shaped Os₃C core with open triangular geometry. The osmium-osmium bonds lengths are
190 2.8757(4) Å [Os(1)-Os(2)] and 2.9111(4) Å [Os(2)-Os(3)], while the non-bonded Os(1)-Os(3) distance
191 is 3.7445(4) Å. There are also ten terminal carbonyls and a bridging hydride across the Os(2)-Os(3)
192 bond. The Os(1)-Os(2)-Os(3) angle is fairly large at 80.647(11)°, compared with that in closed
193 triangular clusters.

194 The use of 1,4-bis(3-thienyl)butadiyne instead of 1,4-bis(2-thienyl)butadiyne seems to completely
195 prohibit the aromatic ring expansion upon coordination to Os₃H₂(CO)₁₀. Therefore, in contrast to the
196 reaction of triosmium clusters with thiophenes, benzothiophene and thietane,¹¹ it is possible that in
197 addition to the hydride transfer from the cluster core to the coordinating ligand, there is also a significant
198 interaction of one of the thiophene sulfur atoms with either the cluster core, or the alkyl carbons, which
199 may trigger the ring expansion as observed for cluster **1**. In the case of 3-thienyl-substitution this
200 pathway becomes unavailable, most likely due to the loss of suitable interaction geometry or distance.

201

202 Thermal decarbonylation of **1**.

203 Refluxing a heptane solution of **1** results in thermal decarbonylation to generate the osmium
204 nonacarbonyl species, [Os₃(μ-H)(CO)₉{μ₃-η³-(C₄H₃S)(C₈H₄S)}] (**4**) and [Os₃(μ-H)₂(CO)₉{μ₃-η¹-η¹-
205 (C₄H₃S)(C₈H₃S)}] (**5**) as orange and red solids, respectively (Scheme 2). Thermal reaction of **1** in
206 refluxing toluene under a hydrogen atmosphere selectively yields the dihydride cluster **5**. Extended
207 reaction times (over 48 hours in refluxing toluene) leads to formation of the dihydrido carbonyl cluster
208 [Os₃H₂(CO)₁₀]. Unfortunately, due to the extent of decomposition, and the small amount of the starting
209 cluster used in this experiment, it was not possible to isolate or characterize the resulting organic
210 products cleaved from the parent cluster **1**.



Scheme 2. Decarbonylation reactions of **1**.

A mass spectrum (FAB) of **4** shows a molecular ion peak at m/z 1040, which suggests the loss of one carbonyl from the parent cluster. The ^1H NMR spectrum exhibits three related doublets in the δ 7.05-7.31 region, which may be assigned as signals from a thiophene group, based on relative coupling values. A single hydride resonance is found at δ -18.6, which is typical for an edge bridging coordination mode. Additionally, two pairs of doublets are observed at δ 7.04 and 6.44 ($J=9.6$), and at δ 3.68 and 3.52 ($J=22.9$). The upper field pair of doublets is very similar to those recorded for cluster **2**, which indicates the formation of a similar sp^3 center bonded to two protons. The formation of this vertex from **1** may be explained by a proton translocation from the aromatic sulfur containing ring, followed by transmetallation of the six-membered heterocycle. This process would lead to the loss of aromaticity, which in turn is supported by the upfield shift of the two resonances from the remaining ring-bound protons, relative to analogous protons of **2**.

The solid state molecular structure of **4** (Table 1, Figure 3) consists of a closed 48-electron triosmium triangular core with nine terminal carbonyls, a bridging hydride spanning the longest metal-metal bond, Os(1)-Os(2) (2.9034(4) Å), and the transformed organic ligand coordinated to all three metal atoms. The ligand is coordinated to the osmium core through five bonds ranging from 2.048(8) Å [C(11)-Os(2)] to 2.324(7) Å [C(16)-Os(3)], with carbon-carbon bonds ranging from 1.275(12) Å [C(13)-C(14)] to 1.527(12) Å [C(15)-C(16)], while the carbon-sulfur bonds are 1.742(10) Å and 1.653(9) Å between C(18)-S(1) and C(21)-S(1), respectively. The coordination mode is very similar to previously reported

species.⁷ As in **1**, the thiophene ring does not deviate significantly from the plane of the fused rings with dihedral angles between the two at only 5.30°.

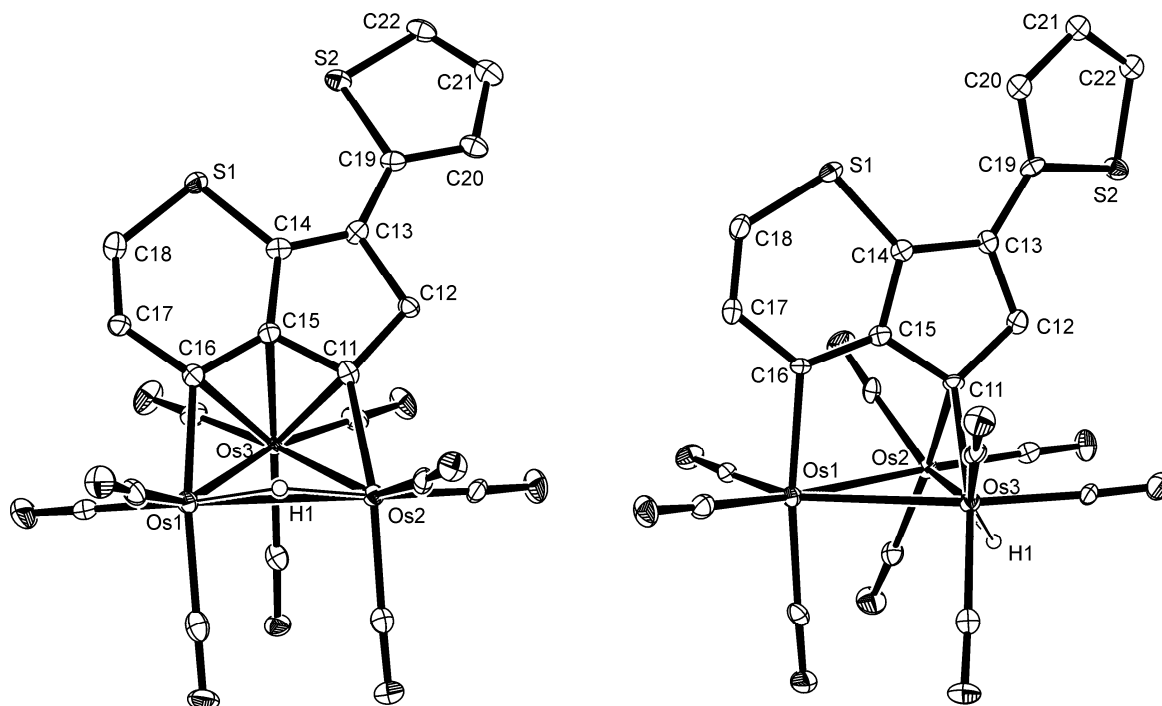


Figure 3. ORTEP plot (30% displacement ellipsoids) of the X-ray structure of **4** (left) and **5** (right). Hydrogen atoms (except H1 and H2) and minor disorder components are omitted for clarity.

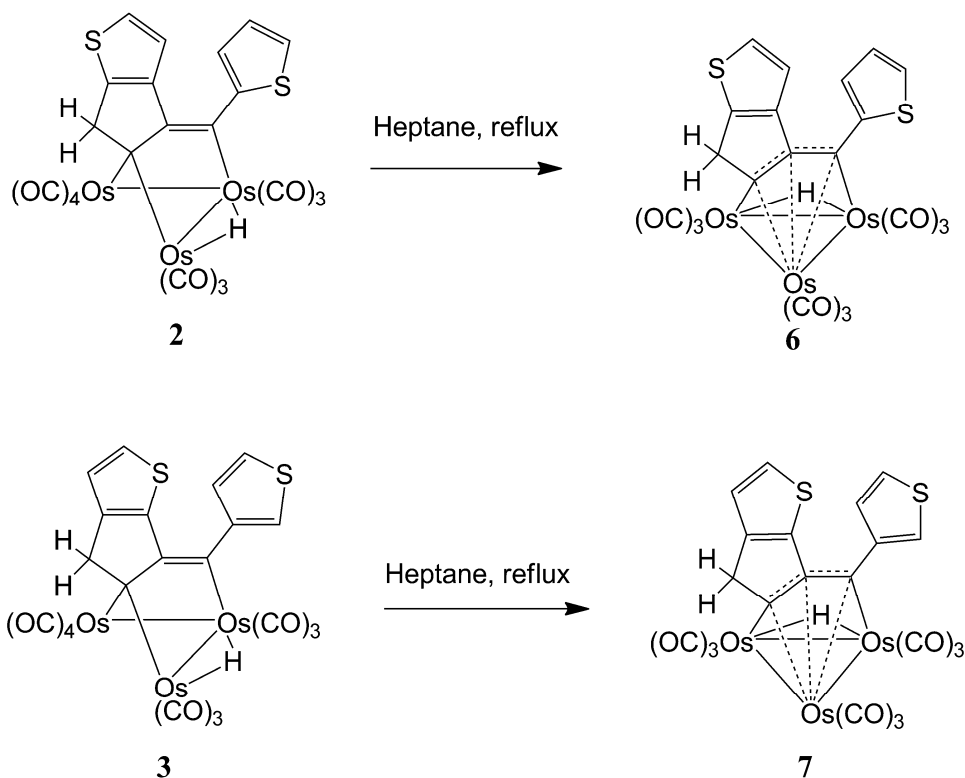
The ¹H NMR spectrum of **5** exhibits a similar set of thiophene ring associated protons as those observed in **4**, at δ 7.51, 7.38, and 7.15. The two hydride resonances (at δ -14.4 and -15.6) found in the ¹H NMR of **5** indicates that a proton transfer from the hydrocarbon ligand has occurred, which has led to the orthometallation of the sulfur containing six-membered ring. In contrast to the structure described for **4**, the aromaticity of the heteroaryl ring has been retained, which is also shown by the relative low-field ¹H resonances of the ring-bound protons (two doublets centered at δ 8.46 and 7.96), and suggests a similar charge separation observed for the parent cluster.

The solid state molecular structure of **5** (Table 1, Figure 3), consists of a closed triosmium triangular core with nine terminal carbonyls and two bridging hydrides between Os(1)-Os(2) and Os(1)-Os(3). The hydrides spans both the longest [Os(1)-Os(3) 3.0238(3) Å] and the shortest [Os(2)-Os(3) 2.7965(3) Å]

osmium-osmium bond. The bis-thiophene ligand has undergone a transformation similar to that in **1** and **4**, with the ligand consisting of a fused five-membered and six-membered sulfur ring linked by C(13)-C(19) 1.441(9) Å to the thiophene ring. This transformed ligand lies almost perpendicular to the plane of the osmium triangle and is bound by C(11)-Os(2) 2.199(6) Å, C(11)-Os(3) 2.188(6) Å and C(16)-Os(1) 2.137(6) Å. The atoms of the lone thiophene ring are disordered over the two sites. The shortest carbon-carbon bond in the fused rings are those between C(17)-C(18) 1.349(10) Å and displays double bond character, the longest carbon-carbon bond has a length of 1.463(9) Å [C(11)-C(15)], while the carbon-sulfur bonds are typical at 1.715(7) for S(1)-C(14) and 1.712(7) for S(1)-C(18).

Thermal decarbonylation of **2** and **3**.

Upon refluxing a solution of **2** in heptane, decarbonylation occurs to yield a single yellow product which was characterised by spectroscopic and single crystal X-ray diffraction as the 48-electron cluster $[\text{Os}_3(\mu\text{-H})(\text{CO})_9\{\mu_3\text{-}\eta^3\text{-(C}_4\text{H}_3\text{S)(C}_8\text{H}_4\text{S)}\}]$ (**6**) (Scheme 3). Under similar conditions, the analogous compound **3** also loses a terminal carbonyl ligand to give pale yellow crystals of $[\text{Os}_3(\mu\text{-H})(\text{CO})_9\{\mu_3\text{-}\eta^3\text{-(C}_4\text{H}_3\text{S)(C}_8\text{H}_4\text{S)}\}]$ (**7**) in quantitative yields (Scheme 3). Unlike in heptane, when the decarbonylation of **3** was performed in toluene the reaction does not proceed cleanly, forming decomposition products in addition to **7**.



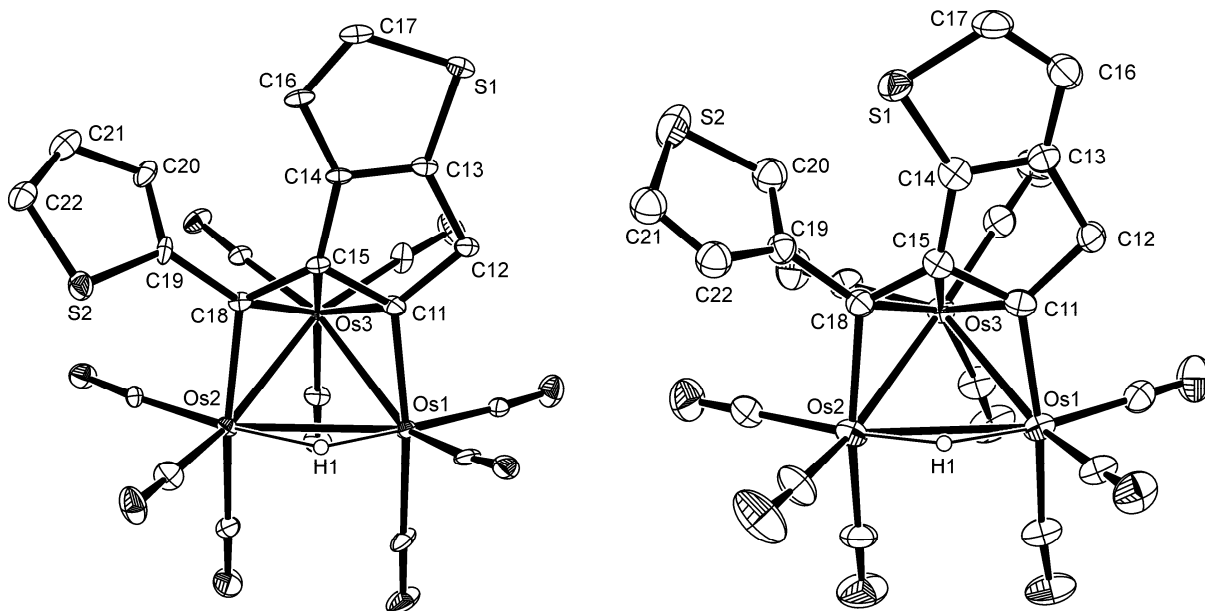
Scheme 3. Thermal decarbonylation of **2** and **3**.

The ^1H NMR spectrum of **6** exhibited a series of multiplets in the aromatic region, two pairs of doublets at δ 3.60 and δ 3.30, along with a single hydride resonance at δ -18.72. All the signals were slightly shifted relative to those in the ^1H NMR spectrum of the parent compound **2**. The FAB-MS spectrum exhibited the molecular ion at m/z 1040, while IR spectrum was characterised by absorptions for terminal $\nu(\text{CO})$. The ^1H NMR spectrum of **7** revealed resonances similar to that found for the parent compound **3**, with a singlet at -18.7 ppm arising due to the hydride proton which is shifted by 1.8 ppm from that exhibited in **3**. The FAB-MS spectrum along with the IR spectrum obtained for **7** were unremarkable exhibiting the expected molecular ion and absorptions for terminal $\nu(\text{CO})$, respectively.

The solid state molecular structure of **6** (Table 2, Figure 5) consists of a closed 48-electron osmium cluster coordinated to nine terminal carbonyls, a bridging hydride, with the transformed ligand being coordinated to all three osmium atoms. The osmium-osmium bond lengths are 2.8012(6) Å [Os(2)-Os(3)], 2.8252(6) Å [Os(1)-Os(3)] and 2.9415(6) Å [Os(1)-Os(2)], with the hydride bridging the longest of the metal-metal bonds. The organic moiety is akin to that in **2** with a fused five-membered ring and a

280 thiophene attached to another thiophene ring. The ligand coordinates to all three osmium atoms with
 281 bonds ranging from 2.076(10) [C(11)-Os(1)] to 2.340(10) [C(15)-Os(3)], with one atom, Os(3) being
 282 coordinated by three atoms of the ligand. A similar coordination mode has been observed in other
 283 triosmium clusters.⁷ Within the organic moiety the shortest bonds are those between C(21)-C(22) at
 284 1.342(17) Å and between C(16)-C(17) at 1.352(15) Å, while the longest bonds are C(11)-C(12)
 285 1.526(14)Å and C(12)-C(13) at 1.513(14) Å. The carbon-sulfur bonds range from 1.693(10) to
 286 1.736(12) Å for C(13)-S(1) and C(17)-S(1) respectively.

287 The solid state molecular structure of **7** (Table 2, Figure 5) is almost identical to **6**, except for the
 288 difference in the position of the sulfur atom in the organic fragment. The organic moiety is similar to
 289 that of **3** and coordinated to all three osmium atoms. The hydride bridges the longest of the osmium-
 290 osmium bonds, Os(1)-Os(2), which is 2.9849(4) Å, while Os(1)-Os(3) and Os(2)-Os(3) distances are
 291 2.8165(4) Å and 2.8157(4) Å respectively. Bonds between the osmium and the coordinated ligand range
 292 from 2.053(7) to 2.348(7) Å, while the carbon-carbon bonds of the ligand range from the shortest at
 293 1.329(13) Å [C(16)-C(17)] to 1.537(10)Å [C(11)-C(12)]. As in **6**, the lone thiophene ring also deviates
 294 significantly from the plane of the fused rings with dihedral angles of 64.0°.



295
 296 **Figure 4.** ORTEP plot (30 % displacement ellipsoids) of the X-ray structure of **6** (left) and **7** (right).
 297 Hydrogen atoms (except H1) and minor disorder components are omitted for clarity.

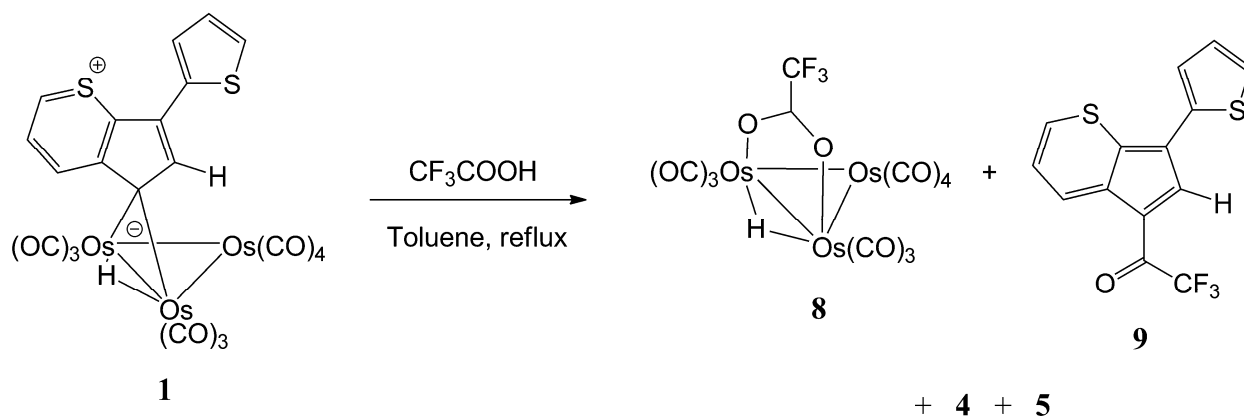
298

299 **Reaction of 1 with trifluoroacetic acid.**

300 Ligand transformations upon anchorage to a cluster surface have yielded a wide variety of organic
301 ligands. While these transformations have been useful in modelling surface reactions, the possibility of
302 clusters to be used as catalysts has been proposed but has not actually found application due to the often
303 strong bonds between the metal surfaces and the chelated ligands. In an effort to simulate a clusters'
304 function as a catalyst, attempts were made to cleave the coordinated organic moiety from cluster **1**.

305 Initial thermal reactions under hydrogen, in the presence of aqueous NaOH, yielded only small
306 amounts of the starting dihydride cluster $\text{Os}_3(\mu\text{-H}_2)(\text{CO})_{10}$ and the stable decarbonylated clusters **4**, **5**
307 and **7**. As bases did not produce the results hoped for, attempts were carried out using concentrated
308 hydrochloric acid, based on reports that alkoxy bridge diols were successfully cleaved from a triosmium
309 cluster.¹⁶ Attempts to cleave the organic moiety were also made utilising trifluoromethyl sulfonic acid.
310 However, both reagents proved to be ineffective.

311 Based on a successful cleavage reaction yielding $[\text{Os}_3\text{H}(\text{CO})_{10}(\text{OCCF}_3)]$ from
312 $[\text{Os}_3\text{H}(\text{CO})_{10}(\text{OSi}\equiv)]$,¹⁷ **1** was reacted with an excess of CF_3COOH at 90 °C. Small amounts of the
313 decarbonylated clusters **4** and **5** were formed but the main products were the previously reported $[\text{Os}_3(\mu\text{-}$
314 $\text{H})(\text{CO})_{10}(\text{O}_2\text{CCF}_3)]$ (**8**)¹⁸ and an intensely colored blue compound, subsequently identified as the
315 thiophene-substituted cyclopentathiopyran derivative $[(\text{C}_4\text{H}_3\text{S})(\text{C}_8\text{H}_4\text{S})\text{OCCF}_3]$ (**9**) cleaved from the
316 parent cluster. The spectroscopic data obtained for **8** were in accordance with the previously reported
317 values.¹⁸ The ^1H NMR spectrum of **9** exhibited resonances similar to that found in **1**, with six
318 resonances in the aromatic region, and a resonance downfield at 9.34 ppm (*ca.* 9.65 ppm found for **1**)
319 due to the protonated carbon of the cyclopentene group fused to the thiopyran. The IR spectrum obtained
320 exhibited $\nu(\text{COO})$ at 1662 cm^{-1} , while the FAB-MS spectrum displayed the expected molecular ion.



Scheme 4. Reaction of **1** with $\text{CF}_3\text{CO}_2\text{H}$.

As the structure of **8** had not been previously reported, a single-crystal X-ray diffraction experiment was carried out. The solid state molecular structure of **8** consists, as expected, of a closed triosmium core with a bridging hydride between the longest osmium-osmium bonds, Os(2)-Os(3) 2.9322(5) Å, and ten terminal carbonyl bonds, three each on Os(2) and Os(3) and four on Os(1). The angles within the metal core range from 53.861(11)° for Os(1)-Os(3)-Os(2) to 67.887(13)° for Os(2)-Os(1)-Os(3). The trifluoroacetic acid moiety bridges the triangular osmium core with O(12) bound to Os(2) and O(11) bound to Os(3) at distances of 2.135(5) and 2.122(6) Å respectively.

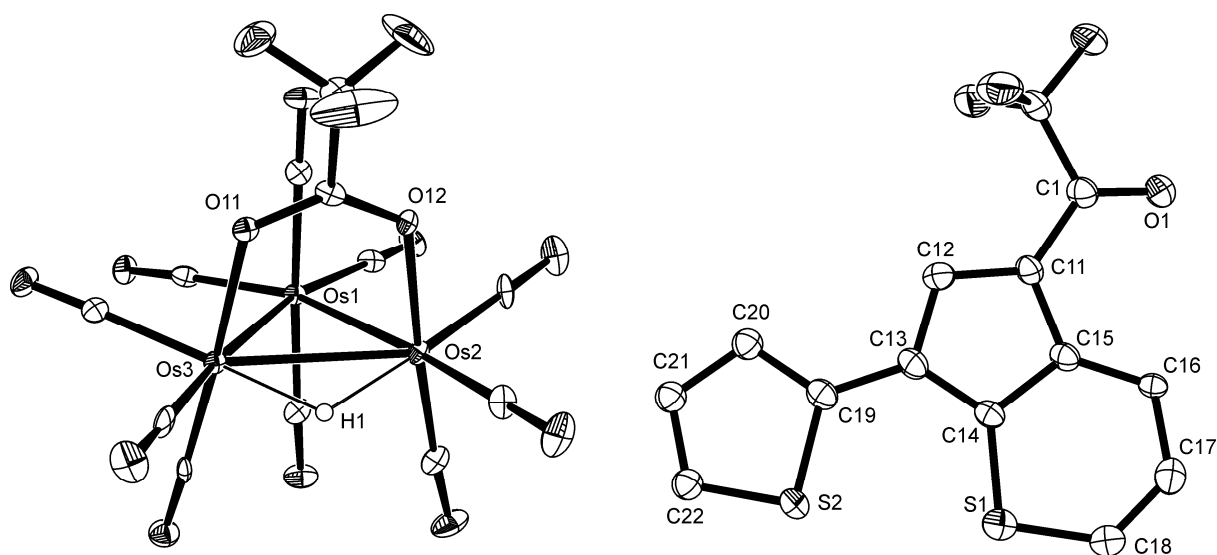


Figure 5. ORTEP plot of the X-ray structure of **8** (left) and **9** (right). Hydrogen atoms (except H1) and minor disorder components are omitted for clarity.

334 **Table 1.** Selected bond lengths (Å) and angles (deg) for **1**, **4**, **5** and **9**.

	1	4	5	9
Os(1)-Os(2)	2.8796(4) 2.971	2.9034(4) 3.072	2.8446(3) 2.924	-
Os(1)-Os(3)	2.8814(3) 2.969	2.7386(4) 2.889	3.0238(3) 3.139	-
Os(2)-Os(3)	2.7765(3) 2.853	2.8199(4) 2.901	2.7965(3) 2.886	-
Os-H(1) ^a	1.87(4) 1.860	1.63(4) 1.813	1.88(5) 1.826	-
Os-H(2) ^a	-	-	1.83(6) 1.813	-
Os-C(CO)	1.904(5)- 1.952(5)	1.851(8)- 1.952(8)	1.905(6)- 1.959(7)	-
Os(2)-C(11)	2.230(5) 2.291	2.048(8) 2.086	2.199(6) 2.243	-
Os(3)-C(11)	2.235(5) 2.289	2.293(7) 2.371	2.188(6) 2.222	-
Os(1)-C(16)	-	2.074(8) 2.124	2.137(6) 2.142	-
Os(3)-C(15)	-	2.302(7) 2.384	-	-
Os(3)-C(16)	-	2.324(7) 2.416	-	-
S(1)-C(14)	1.690(5) 1.728	1.744(8) 1.763	1.715(7) 1.724	1.693(5) 1.732
S(1)-C(18)	1.689(6) 1.721	1.684(8) 1.747	1.712(7) 1.719	1.664(5) 1.723
Os(2)-Os(1)-Os(3)	57.625(7) 57.43	59.890(10) 58.15	56.821(8) 56.71	-
Os(1)-Os(2)-Os(3)	61.220(8) 61.24	57.152(9) 57.76	64.821(9) 65.42	-
Os(2)-Os(3)-Os(1)	61.155(9) 61.33	62.958(10) 64.09	58.357(8) 57.87	-

a. averaged value

338 **Table 2.** Selected bond lengths (Å) and angles (deg) for **2**, **3**, **6** and **7**.

	2	3	6	7
Os(1)-Os(2)	2.8702(3) 2.956	2.8757(4) 2.958	2.9415(6) 3.061	2.9849(4) 3.069
Os(1)-Os(3)	-	-	2.8252(6) 2.912	2.8165(4) 2.910
Os(2)-Os(3)	2.9139(3) 2.989	2.9111(4) 2.991	2.8012(6) 2.880	2.8157(4) 2.879
Os-H(1) ^a	1.82(4) 1.826	1.83(16) 1.827	1.71(7) 1.805	1.69(4) 1.805
Os-C(CO)	1.895(6)- 1.950(6)	1.910(8)- 1.947(8)	1.907(11)- 1.979(11)	1.890(8)- 1.952(8)
Os(1)-C(11)	2.198(5) 2.240	2.197(6) 2.241	2.076(10) 2.087	2.053(7) 2.084
Os(3)-C(11)	2.317(5) 2.236	2.325(7) 2.366	2.261(11) 2.331	2.299(7) 2.343
Os(3)-C(15)	2.290(5) 2.355	2.287(7) 2.359	2.340(10) 2.414	2.348(6) 2.403
Os(2)-C(18)	2.161(5) 2.199	2.151(6) 2.197	2.119(10) 2.135	2.115(7) 2.127
Os(3)-C(18)	2.212(5) 2.262	2.216(6) 2.261	2.329(9) 2.400	2.309(7) 2.412
S(1)-C(13)	1.726(5) 1.725	1.720(7) ^c 1.735	1.693(10) 1.723	1.710(8) ^b 1.735
S(1)-C(17)	1.721(6) 1.751	1.738(9) 1.741	1.736(12) 1.749	1.730(9) 1.742
Os(2)-Os(1)-Os(3)	-	-	58.081(14) 57.57	57.983(9) 57.50
Os(1)-Os(2)-Os(3)	81.046(8) 81.07	80.641(10) 81.02	58.880(14) 58.61	58.009(9) 58.48
Os(2)-Os(3)-Os(1)	-	-	63.039(14) 63.82	64.008(10) 64.03

a. averaged value b. S(1)-C(14)

Computational Studies

The credible location of hydrides using X-ray crystallography is notoriously challenging, particularly in the presence of very heavy atoms. Thus, to support the formulation of the osmium complexes, DFT calculations were performed to confirm the geometry, in particular whether the location of the hydride(s) was correct. Within the expected tolerances, the calculated structures were in good agreement with those obtained from the X-ray experiment (Table 1 and 2). The Os-Os and Os-C distances in the calculated structures are slightly longer than those in the solid state; this feature is found for all complexes. In cases where the experimental geometries were suspect (*eg.* in **4**, C(13)-C(14) is unusually short at 1.288(11) Å) the calculated bond parameters seemed more reasonable (1.365 Å). The calculated hydride locations also matched well with those obtained from the X-ray experiment, and this point, together with the fact that the non-hydrogen atomic positions also show good agreement between experiment and theory, suggest that the formulation of the compounds is correct.

Conclusions.

In summary, we have studied the coordination of 2- and 3-thienyl substituted diynes to the triosmium cluster $\text{Os}_3\text{H}_2(\text{CO})_{10}$. In the present study the aromatic endgroups are shown to undergo significant transformations upon coordination to the triosmium core, including intramolecular cyclizations and formation of novel heteroaryl subunits. Although the reaction mechanisms for the transformations remain unclear, it is likely that the availability of the sulfur atom for coordination to the metal center, and the presence of the osmium bound bridging hydrides, are key factors which determine the type of the ligand transformation.

Following the common trend for triosmium clusters, compound **1** may be thermally decarbonylated to yield the osmium nonacarbonyl species **4** and **5**, which are not thermally interconvertible. Compounds **2** and **3** can be decarbonylated to give the nonacarbonyl compounds **6** and **7** respectively. In the case of **1**,

the transformed organic moiety could be removed from the osmium cluster by treatment with trifluoroacetic acid.

Experimental Section

General Procedures

The parent osmium cluster $\text{Os}_3\text{H}_2(\text{CO})_{10}$, 1,4-bis(2-thienyl)butadiyne and 1,4-bis(3-thienyl)butadiyne were prepared by literature methods.¹⁹ All other reagents were of analytical grade and were used as received. The compounds 2,7-dimethylocta-3,5-diyne-2,7-diol and $[\text{PdCl}_2(\text{PPh}_3)_2]$ were purchased from Lancaster, CuI and 2- and 3-bromothiophenes from Avocado, benzyltriethylammonium chloride from Aldrich, and $\text{Os}_3(\text{CO})_{12}$ from Strem Chemicals. The reactions were carried out under an nitrogen atmosphere using freshly distilled solvents. All manipulations of the products were performed in air. Thin layer chromatography was performed on commercial 20 x 20 cm plates (Aldrich) covered with Merck silica gel 60 F254 to 0.25 or 1.0 mm thickness. Column chromatography separations were performed using 2x40 cm column and SG 60 silica gel (Aldrich).

Infrared spectra were measured using a Nicolet Avatar 360 FTIR spectrometer from dichloromethane solutions. ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker AV300 spectrometer or a Bruker AV500 spectrometer using CDCl_3 as a solvent, at room temperature unless otherwise specified. In the spectrum of **1**, chemical shifts were assigned with the aid of HMQC and HMBC experiments.

Crystallographic Methods. The diffraction data were collected using a Nonius Kappa CCD diffractometer using standard $\text{MoK}\alpha$ radiation or an Apex II diffractometer at Station 9.8, Daresbury SRS. Data were processed using the supplied Nonius or Bruker software. Structure solution, followed by full-matrix least squares refinement was performed using Sir97,²⁰ and/or SHELX²¹ under the WinGX²² package. Hydrides were located and restrained to be symmetrically bridging, but otherwise freely refined. All other hydrogen atoms were placed in idealized positions. The crystallographic data for compounds **1-9** are collected in Tables 3 and 4.

390 **Computational Studies.** All calculations were performed using the B3LYP²³ hybrid density
391 functional under the Gaussian 09 package.²⁴ Geometry optimisations ("tight" convergence criteria) were
392 performed using a quasi-relativistic pseudopotential and associated basis set (SDD) for osmium,²⁵ and a
393 6-31G(d,p)²⁶ basis set for all other atoms. Frequency calculations were performed at the optimised
394 geometries to confirm the nature of the stationary points. Free energies are reported for a temperature of
395 298 K and a pressure of 1 atm.

396 **Preparation of [Os₃(μ -H)(CO)₁₀{ μ - η -(C₄H₃S)(C₈H₄S)}] (1) and [Os₃(μ -H)(CO)₁₀{ μ_3 - η^2 - η^1 - η^1 -
397 (SC₇H₄)C(SC₄H₃)}] (2).**

398 A solution of Os₃H₂(CO)₁₀ (200 mg, 0.21 mmol) and 1,4-bis(2-thienyl)butadiyne (**L1**) (47 mg, 0.22
399 mmol) in dichloromethane (40 mL) was stirred for 12 h under nitrogen, at room temperature. The
400 solvent was removed *in vacuo* and the residue was subjected to preparative TLC (eluent:
401 hexane/dichloromethane 3:1). Two fractions were obtained: a minor yellow-orange band with high R_f
402 (51 mg, 35%) and a major green band, **1** (135 mg, 55 %) with lower R_f. Evaporation of a
403 dichloromethane solution of **1** yielded dark green crystals suitable for X-ray diffraction study. The
404 orange material could not be completely separated, but slow evaporation of a solution in
405 dichloromethane /hexane gave small single crystals of **2** suitable for X-ray diffraction studies and
406 spectroscopic analysis.

407

408 [Os₃(μ -H)(CO)₁₀{ μ - η -(C₄H₃S)(C₈H₄S)}] (**1**). IR (CH₂Cl₂), ν (CO)/cm⁻¹: 2095(s), 2086(sh), 2060(vs),
409 2052(vs), 2039(sh), 2007(vs), 1998(sh), 1976(m).

410 ¹H NMR (500.1 MHz, CDCl₃, 220K) δ 9.60 (s, H12), 8.38 (d, ³J=8.5 Hz, H18), 7.95 (dd, ³J=8.5, 8.0
411 Hz, H17), 7.90 (d, ³J=8.0 Hz, H16), 7.54 (d, ³J=3.5 Hz, H20), 7.43 (d, ³J=5 Hz, H22), 7.23 (dd, ³J=5.0,
412 3.5 Hz, H21), -14.90 (s, Os-H).

413 ¹³C NMR (125.8 MHz, CDCl₃, 220K) δ 188.89 (CO), 182.90 (CO), 180.92 (CO), 178.41 (CO),
414 178.29 (C12), 176.88 (CO), 171.75 (CO), 164.69 (C15), 142.97 (C16), 142.55 (C14), 136.60 (C19),
415 133.83 (C18), 128.43 (C21), 125.10 (C13), 123.96 (C22), 122.90 (C20), 121.79 (C17), 63.07 (C11).

416 FAB MS (m/z) 1068 $[M]^+$. Anal. Calcd for $C_{22}H_8O_{10}S_2Os_3$: C, 24.7; H, 0.75. Found: C, 24.8; H, 0.8.

417

418 $[Os_3(\mu-H)(CO)_{10}\{\mu_3-\eta^2-\eta^1-\eta^1-(SC_7H_4)C(SC_4H_3)\}]$ (**2**).

419 IR (CH_2Cl_2), $\nu(CO)/cm^{-1}$: 2111(w), 2083(m), 2058(vs), 2027(vs), 2006(s), 1983(sh).

420 1H NMR (500.1 MHz, CD_2Cl_2 , 298K) δ 7.17 (br, 3H, C_4H_3S), 7.13 (d, $J=5.1$ Hz, 1H, C_4H_2S), 5.97

421 ($J=5.1$ Hz, 1H, C_4H_2S), 3.54 (AB, $J\sim 22$ Hz, 2H, CH_2), -16.94 (s, 1H, Rh-H).

422 1H NMR (500.1 MHz, CD_2Cl_2 , 228K) δ 7.46 (d, $^3J=5.1$ Hz, 1H, H_m), 7.27 (dd, $J=5.2$, 3.4 Hz, 1H,

423 H_M), 7.20 (d, $J=3.4$ Hz, 1H, H_M), 7.12 (d, $^3J=5.1$ Hz, 1H, H_{M+m}), 7.04 (d, $^3J=5.2$ Hz, 1H, H_M), 6.93 (dd,

424 $J=5.2$, 3.2 Hz, 1H, H_m), 6.60 (d, $^3J=3.2$ Hz, 1H, H_m), 5.86 (d, $J\sim 5$ Hz, 1H, H_m), 5.85 (d, $J\sim 5$ Hz, 1H,

425 H_M), 3.50 (AB, $J\sim 23$ Hz, CH_2 : $M+m$), -17.00 (s, 1H, Rh- H_M), -17.08 (s, 1H, Rh- H_m). H_M = major isomer,

426 H_m = minor isomer.

427 FAB MS (m/z) 1040 $[M-CO]^+$. Anal. Calcd for $C_{22}H_8O_{10}S_2Os_3$: C, 24.7; H, 0.75. Found: C, 24.6; H,

428 0.9.

429 **Preparation of $[Os_3(\mu-H)(CO)_{10}\{\mu-\eta-(C_4H_3S)(C_8H_4S)\}]$ (**3**).**

430 A solution of $Os_3H_2(CO)_{10}$ (143 mg, 0.17 mmol) and 1,4-bis(3-thienyl)butadiyne (**L2**) (40 mg, 0.19

431 mmol) in dichloromethane (40 mL) was stirred at room temperature under nitrogen. The reaction was

432 monitored by TLC, which showed that most of the parent cluster was consumed after 48 hours. The

433 resulting yellow solution was concentrated under reduced pressure, and separated *via* preparative TLC

434 (eluent: dichloromethane/hexane 1:6). The major yellow band was collected to give **3** as a yellow solid

435 (120 mg, 70%). Crystals suitable for single-crystal X-ray diffraction were grown by recrystallization of a

436 chloroform solution of **3** at -20 °C.

437 $[Os_3(\mu-H)(CO)_{10}\{\mu-\eta-(C_4H_3S)(C_8H_4S)\}]$ (**3**). IR (CH_2Cl_2), $\nu(CO)/cm^{-1}$: 2110(m), 2081(vs), 2056(vs),

438 2024(vs), 2001(s), 1974(sh). 1H NMR (300.1 MHz, $CDCl_3$), δ 7.37 (dd, $^3J=4.8$ Hz, $^4J=3.0$ Hz, 1H), 7.28

439 (d, $^3J=4.8$ Hz, 1H), 7.01 (dd, $^3J=4.8$ Hz, $^4J=1.2$ Hz, 1H), 6.93 (d, $^3J=4.8$ Hz, 1H), 6.77 (dd, $^4J=3.0$ Hz,

440 $^4J=1.5$ Hz, 1H), 4.24 (d, $^2J=22$ Hz, 1H), 4.04 (d, $^2J=22$ Hz, 1H), -16.9 (s, 1H). FAB MS (m/z) 1068
441 $[M]^+$. Anal. Calcd for $C_{22}H_8O_{10}S_2Os_3$: C, 24.7; H, 0.75. Found: C, 24.8; H, 0.80.

442 **Thermal decarbonylation of 1 to give $[Os_3(\mu-H)(CO)_9\{\mu_3-\eta^3-(C_4H_3S)(C_8H_4S)\}]$ (4) and $[Os_3(\mu-$
443 $H)_2(CO)_9\{\mu_3-\eta^1-\eta^1-(C_4H_3S)(C_8H_3S)\}]$ (5).**

444 A solution of **1** (60 mg, 0.056 mmol) in heptane (35 mL) was heated to 65 °C under nitrogen, and the
445 temperature maintained for 3h. The resulting orange solution was cooled to room temperature and the
446 solvent removed under reduced pressure. Purification of was performed using preparative TLC (eluent:
447 dichloromethane/hexane 3:7). The orange product (high R_f) was recrystallised from a dichloromethane
448 solution to give **4** as a microcrystalline solid (23 mg, 40 %). Evaporation of a concentrated chloroform
449 solution at -20 °C of the red solid yielded **5** as dark red crystals (22 mg, yield 38 %).

450 $[Os_3(\mu-H)(CO)_9\{\mu_3-\eta^3-(C_4H_3S)(C_8H_4S)\}]$ (**4**). IR (CH_2Cl_2), $\nu(CO)/cm^{-1}$: 2102(s), 2059(vs), 2022(s),
451 2012(sh), 1991(m), 1961(m). 1H NMR (300.1 MHz, $CDCl_3$), δ 7.31 (dd, $^3J=5.1$ Hz, $^4J=1.1$ Hz, 1H),
452 7.13 (dd, $^3J=3.7$ Hz, $^3J=5.1$ Hz, 1H), 7.10 (dd, $^3J=3.7$ Hz, $^4J=1.1$ Hz, 1H), 7.04 (d, $^3J=9.6$ Hz, 1H), 6.44
453 (d, $^3J=9.6$ Hz, 1H), 3.68 (d, $^2J=23$ Hz, 1H), 3.52 (d, $^2J=23$ Hz, 1H), -18.58 (s, 1H). FAB MS (m/z) 1040
454 $[M]^+$. Anal. Calcd for $C_{21}H_8O_9S_2Os_3$: C, 24.27; H, 0.78. Found: C, 24.4; H, 0.66.

455 $[Os_3(\mu-H)_2(CO)_9\{\mu_3-\eta^1-\eta^1-(C_4H_3S)(C_8H_3S)\}]$ (**5**). IR (CH_2Cl_2), $\nu(CO)/cm^{-1}$: 2099(m), 2086(sh),
456 2066(vs), 2055(sh), 2030(m), 2017(sh), 1989(sh). 1H NMR (300.1 MHz, $CDCl_3$), δ 8.46 (d, $^3J=8.6$ Hz,
457 1H), 7.96 (d, $^3J=8.6$ Hz, 1H), 7.84 (s, 1H), 7.51 (dd, $^3J=3.7$, $^4J=1.1$ Hz, 1H), 7.38 (dd, $^3J=5.1$, $^4J=1.1$ Hz,
458 1H), 7.15 (dd, $^3J=5.1$, $^3J=3.7$ Hz, 1H), -14.38 (s, 1H), -15.58 (s, 1H). FAB MS (m/z) 1040 $[M]^+$. Anal.
459 Calcd for $C_{21}H_8O_9S_2Os_3$: C, 24.27; H, 0.78. Found: C, 24.1; H, 0.85.

460 **Thermal decarbonylation of 2 to give $[Os_3(\mu-H)(CO)_9\{\mu_3-\eta^3-(C_4H_3S)(C_8H_4S)\}]$ (6).**

461 A heptane solution of **2** (30 mL, 30 mg, 0.03 mmol) was heated at 90 °C under a nitrogen atmosphere
462 for 27 h. The resulting yellow solution was cooled to room temperature, and the solvent removed under
463 reduced pressure. Purification of the product was performed using preparative TLC (eluent:
464 dichloromethane/hexane 1:4) resulting in **2** (6mg, 20%) and the decarbonylated yellow product **6** (7mg,

24 %). Crystals suitable for single crystal X-ray diffraction were grown by solvent diffusion from a dichloromethane/heptane mixture.

IR (CH₂Cl₂), $\nu(\text{CO})$ / cm⁻¹: 2097(s), 2072(vs), 2045(s), 2018(sh), 2004(s), 1990(sh). ¹H NMR (300.1 MHz, CDCl₃) δ 7.49 (dd, ³*J*=4.8, ⁴*J*=3.2 Hz, 1H), 7.20 (d, ³*J*=4.8 Hz, 1H), 7.17 (dd, ³*J*=4.8, ⁴*J*=1.2 Hz, 1H), 7.03 (dd, ⁴*J*=2.7, ⁴*J*=1.2 Hz, 1H), 6.81 (d, ³*J*=4.8 Hz, 1H), 3.60 (d, ²*J*=22 Hz, 1H), 3.30 (d, ²*J*=22 Hz, 1H), -18.72 (s, 1H). FAB MS (*m/z*) 1040 [M]⁺. Owing to the small amount of the product, elemental analysis was not acquired for cluster **6**.

Thermal decarbonylation of 3 to give [Os₃(μ -H)(CO)₉{ μ_3 - η^3 -(C₄H₃S)(C₈H₄S)}] (7).

A heptane solution of **3** (35 mL, 100 mg, 0.09 mmol) was heated at 80 °C for 14 h under a nitrogen atmosphere. The resulting yellow solution was cooled to room temperature and the solvent removed under reduced pressure. Purification by preparative TLC (eluent: dichloromethane/hexane 1:4) and subsequent crystallization from a dichloromethane solution yielded pale yellow crystals of **7** (77 mg, 79 %) suitable for single crystal X-ray diffraction.

Compound **7** was also formed (in *ca.* 30 % yield) when **3** was refluxed in toluene (40 mL) under H₂ atmosphere for 14 h. The reaction mixture contained some starting material, **3**, a small amount of Os₃H₂(CO)₁₀, and a dark-brown decomposition product

IR (CH₂Cl₂), $\nu(\text{CO})/\text{cm}^{-1}$: 2097(s), 2071(vs), 2045(s), 2016(sh), 2002(s), 1991(sh). ¹H NMR (300.1 MHz, CDCl₃) δ 7.49 (dd, ³*J*=4.8, ⁴*J*=3.2 Hz, 1H), 7.20 (d, ³*J*=4.8 Hz, 1H), 7.17 (dd, ³*J*=4.8, ⁴*J*=1.2 Hz, 1H), 7.03 (dd, ⁴*J*=2.7, ⁴*J*=1.2 Hz, 1 H), 6.81 (d, ³*J*=4.8 Hz, 1H), 3.60 (d, ²*J*=22 Hz, 1H), 3.30 (d, ²*J*=22 Hz, 1H), -18.72 (s, 1H). FAB MS (*m/z*) 1040 [M]⁺. Anal. Calcd for C₂₁H₈O₉S₂Os₃: C, 24.27; H, 0.78. Found: C, 24.7; H, 0.9.

Reaction of 1 with trifluoroacetic acid to give [Os₃(μ -H)(CO)₉{ μ_3 - η^3 -(C₄H₃S)(C₈H₄S)}] (4), [Os₃(μ -H)₂(CO)₉{ μ_3 - η^1 - η^1 -(C₄H₃S)(C₈H₃S)}] (5), [Os₃(μ -H)(CO)₁₀(O₂CCF₃)] (8) and [(C₄H₃S)(C₈H₄S)OCCF₃] (9).

489 Trifluoroacetic acid (CF_3COOH) (99 %, 1.5 mL) was added dropwise to a solution of **1** (50 mg, 0.05
490 mmol) in toluene (50 mL) and the dark green mixture was heated to 90 °C under nitrogen for 3h and
491 monitored by TLC. The resulting dark violet solution was cooled to room temperature, and the solvent
492 removed under reduced pressure. Purification by preparative TLC (eluent: dichloromethane/hexane 1:3)
493 yielded small amounts of the expected decarbonylated clusters **4** (3 mg, 6 %), and **5** (10 mg, 21 %), as
494 well as the yellow product **8** (high R_f , 21 mg, 46 %), and an intensely deep blue colored product **9** (low
495 R_f , 10 mg, 68 %). Crystals suitable for single crystal X-ray diffraction of **8** were grown by slow
496 evaporation from a dichloromethane solution at -20 °C. Crystals suitable for single crystal X-ray
497 diffraction of **9** were grown from slow evaporation of dichloromethane and chloroform solutions under
498 nitrogen at -20 °C.

499 $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\text{O}_2\text{CCF}_3)]$ (**8**) The spectroscopic data for **8** were in accordance with the previously
500 reported values.¹⁷

501 $[(\text{C}_4\text{H}_3\text{S})(\text{C}_8\text{H}_4\text{S})\text{OCCF}_3]$ (**9**) IR (CH_2Cl_2), $\nu(\text{CO})/\text{cm}^{-1}$: not observed; $\nu(\text{COO})/\text{cm}^{-1}$: 1662(m). ^1H
502 NMR (300.1 MHz, CDCl_3) δ 9.34 (d, $^3J=8.1$ Hz, 1H), 8.28 (m, 1H), 8.24 (d, $^3J=8.7$ Hz, 1H), 7.71 (dd,
503 $^3J=8.7$, $^3J=8.1$ Hz, 1H), 7.40 (dd, $^3J=3.6$ Hz, $^4J=0.9$ Hz, 1H), 7.29 (dd, $^3J=5.0$ Hz, $^4J=0.6$ Hz, 1H), 7.12
504 (dd, $^3J=5.0$, $^4J=3.6$ Hz, 1H). FAB MS (m/z) 312 $[\text{M}]^+$. Anal. Calcd for $\text{C}_{14}\text{H}_7\text{F}_3\text{OS}_2$: C, 53.84 H, 2.26.
505 Found: C, 54.0 H, 2.3.

506

	1	2	3	4 · CH₂Cl₂
λ , Å	0.68960	0.68960	0.71073	0.71073
temp, K	100	100	150	150
fw	1067.00	1067.00	1067.00	1123.92
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	P -1	P 2 ₁ /c	P 2 ₁ /c	P 2 ₁ /n
a, Å	9.3029(8)	9.3559(7)	9.5820(1)	10.1345(1)
b, Å	9.5330(8)	12.9130(9)	12.8410(2)	10.0843(1)
c, Å	15.6280(13)	21.0946(15)	20.8926(3)	24.6832(3)
α , °	76.505(1)	90	90	90
β , °	86.052(1)	101.1786(7)	99.667(1)	92.779(1)
γ , °	65.963(1)	90	90	90
V, Å ³	1230.29(18)	2500.1(3)	2534.17(6)	2519.64(5)
Z	2	4	4	4
D_{calc} , g/cm ³	2.880	2.835	2.797	2.963
cryst size, mm	0.06 x 0.06 x 0.03	0.03 x 0.01 x 0.01	0.3 x 0.3 x 0.3	0.25 x 0.13 x 0.10
μ , mm ⁻¹	15.679	15.431	15.223	15.522
θ limits, deg	1.31-29.75	3.50-29.51	2.98-27.47	3.71-28.68
N (unique)	7327	7605	5794	6002
R(int)	0.0262	0.0540	0.0776	0.1115
N ($I > 2\sigma(I)$)	6447	6767	5190	5310
no. of params	337	340	334	348
$R1$ ($I > 2\sigma(I)$)	0.0310	0.0314	0.0357	0.0417
$wR2$ (all data)	0.0651	0.0701	0.0952	0.1047
goodness of fit	1.053	1.053	1.143	1.062

509 **Table 4.** Crystallographic data for **5-9**.

	5 · CH ₂ Cl ₂	6	7	8	9
λ , Å	0.71073	0.71073	0.71073	0.71073	0.71073
temp, K	150	150	299	150	150
fw	1123.92	1038.99	1038.99	964.73	312.32
cryst syst	triclinic	monoclinic	triclinic	orthorhombic	monoclinic
space group	P -1	P 2 ₁ /c	P -1	P bca	P 2 ₁ /n
a, Å	8.0318(1)	7.1181(1)	9.7914(1)	14.4142(3)	5.0930(4)
b, Å	13.0303(2)	9.3994(2)	9.8672(2)	16.1384(4)	13.0000(10)
c, Å	13.3423(2)	35.2309(7)	14.7041(3)	14.1976(4)	19.9540(16)
α , °	93.248(1)	90	101.234(1)	90	90
β , °	97.560(1)	95.504(1)	96.840(1)	90	95.239(4)
γ , °	101.826(1)	90	115.936(1)	90	90
V, Å ³	1349.80(3)	2346.29(8)	1218.98(4)	3302.68(14)	1249.68(17)
Z	2	4	2	8	4
D_{calc} , g/cm ³	2.765	2.941	2.831	3.880	1.660
cryst size, mm	0.3 x 0.05 x 0.05	0.25 x 0.03 x 0.03	0.30 x 0.10 x 0.05	0.13 x 0.10 x 0.08	0.25 x 0.08 x 0.05
μ , mm ⁻¹	14.487	16.435	15.831	23.129	0.453
θ limits, deg	3.01-27.51	4.11-27.35	3.71-30.09	3.79-31.34	3.13-25.03
N (unique)	6186	5230	7117	4301	2205
R(int)	0.0818	0.1356	0.0798	0.0900	0.2113
N ($I > 2\sigma(I)$)	5460	3916	5999	3274	1236
no. of params	347	319	316	275	178
$R1$ ($I > 2\sigma(I)$)	0.0398	0.0485	0.0508	0.0402	0.0679
$wR2$ (all data)	0.1047	0.1019	0.1377	0.0942	0.1800
goodness of fit	1.030	1.053	1.041	1.000	1.037

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513

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517 **Supporting Information Available:** Tables of selected bond parameter data for compounds **1-9**
518 together with bond parameter data obtained from the DFT calculations. Calculated atomic coordinates
519 for the optimised structures of compounds **1-9**, **L1**, **L2** and Os₃(H)₂(CO)₁₀ (xyz format). X-ray atomic
520 coordinates, thermal parameters, bond distances, and angles for compounds **1 – 9** (cif format). This
521 material is available free of charge via the Internet at <http://pubs.acs.org>.

522

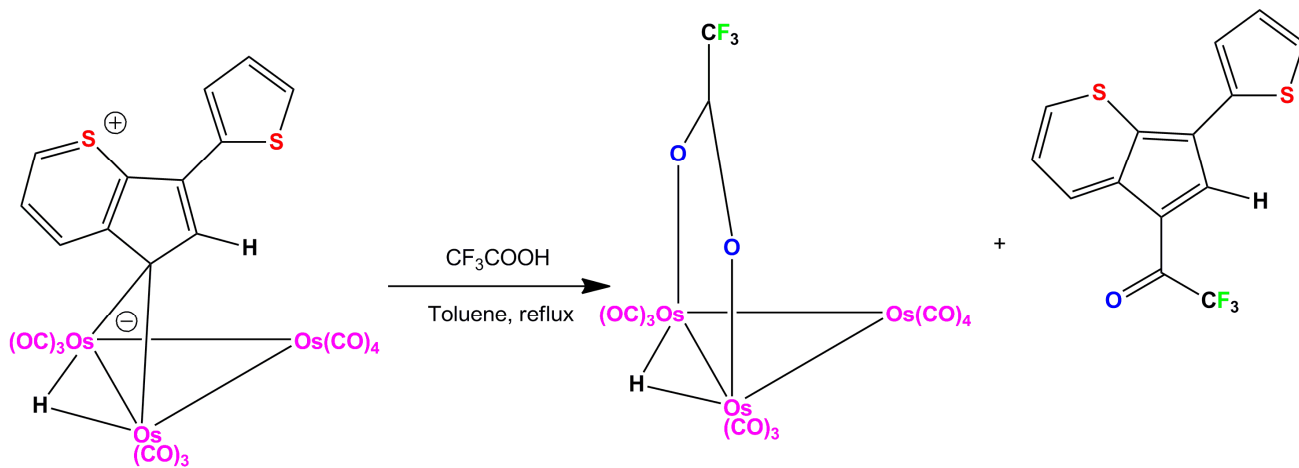
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